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Anion Surfactants as Corrosion Inhibitors for Aluminum Dissolution in HCl Solutions

*G.Y. Elewady** *and I.A.El-Said and A.S.Fouda*

Department of Chemistry, Faculty of Science, El-Mansoura Univeristy, El-Mansoura - 35516, Egypt
*E-mail: Ghadaelewady@yahoo.com

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The role of some surfactants in the corrosion of Al in 1 M HCl has been studied using weight loss and galvanostatic polarization techniques. Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. The inhibition efficiency was found to increase with increasing inhibitor concentration and decreased with increasing temperature which is due to the fact, that the rate of corrosion of Al is higher than the rate of adsorption. The adsorption of the these compounds on the metal surface is found to obey Freundlich adsorption isotherm. The inhibiting action of these compounds are considerably enhanced by the addition of KI, due to the increase of the surface coverage and therefore indicate the joint adsorption of these compounds and iodide ions. Thermodynamic parameters for adsorption and activation processes were determined. Galvanostatic polarization data indicated that these compounds act as mixed-type inhibitors .Results obtained from the two techniques are in good agreement.

Keywords: corrosion, Al ,anionic surfactants, HCl

1. INTRODUCTION

Aluminum and its alloys have a remarkable economic and attractive materials for engineering applications owing to its low cost, light weight, high thermal and electrical conductivity. The interest of the materials arises from their importance in recent civilization. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media[1]. To prevent the attack of acid, it is very important to add a corrosion inhibitor to decrease the rate of Al dissolution in such solutions. Thus, many studies concerning the inhibition of Al corrosion using organic substances are conducted in acidic and basic solutions [2-6].

The present study aimed to investigate the efficiency of some surfactants as corrosion inhibitors for Al in acidic media. An attempt was also made to clarify the effects of concentration and temperature on the inhibition efficiency of the studied inhibitors.

2. EXPERIMENTAL PART

The experiments were performed with aluminum sheets having the chemical composition given in Table (1).

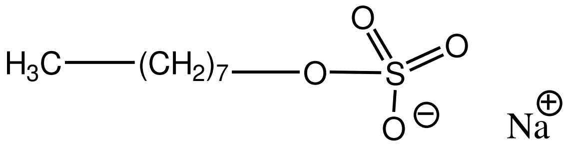
Table 1. Chemical composition (weight %) of aluminum.

Element	Zn	Ti	Si	Cu	Fe	Cr	Ni	Al
Weight	0.08	0.03	0.20	0.02	0.20	0.04	0.04	rest

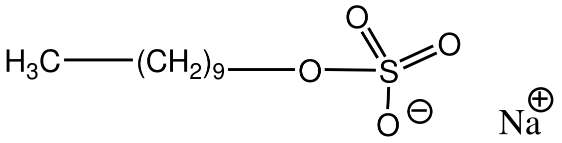
The measurements were performed in 1 M HCl without and with the presence of the investigated surfactants in the concentration range ($1x10^{-6}$ to$11x10^{-6}$M). The name and molecular structures of the surfactants are:

Some anion surfactant as corrosion inhibitors for Al dissolution in hydrochloric acid solution:

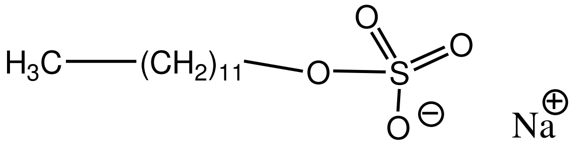
a- Octyl sulphate sodium salt .



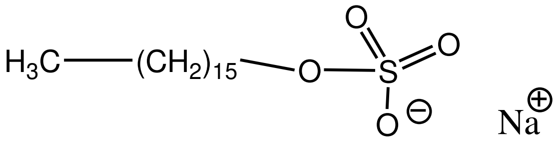
b - Decyl sulphate sadium salt .



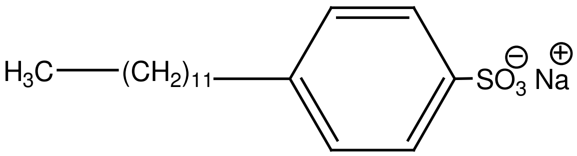
c - Dodecyl sulphate sodium salt.



d - Hexadecyl sulphate sodium salt.



e - Dodecyl benzene sulfonate.



Two different techniques have been employed for studying the inhibition of corrosion of aluminum by these compounds, these are:

i) Chemical technique (Weight loss method)

Aluminum sheets were cut into 2 x 2 cm. They were mechanically polished with emery paper (a coarse paper was used initially and then progressively finer grades were employed), ultrasonically degreased in alkaline degreasing mixture [7], washed with distilled water and finally dried between filter papers and weighed. Aluminum pieces were immersed in 100 ml of the test solution with and without the inhibitors for 30 min. After the test, the pieces were removed, washed with distilled water, dried as before and weighed again. The weight loss of the metal in the corrosive solution is given by:

$$\Delta W = W_1 - W_2 \quad (1)$$

where W_1 and W_2 are the weight of metal before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (% IE) and the degree of surface coverage (θ) of the investigated surfactant compounds were calculated from the following equations:

$$\% \, IE = [1 - (\Delta W_{inh} / \Delta W_{free})] \times 100 \quad (2)$$

$$\theta = [1 - (\Delta W_{inh} / \Delta W_{free})] \quad (3)$$

where ΔW_{free} and ΔW_{inh} are weight losses of metal per unit area in absence and presence of inhibitor at given time period and temperature, respectively.

ii) Electrochemical technique (Galvanostatic polarization method)

Aluminum electrodes were cut from the aluminum sheets. The electrodes were of dimensions 1cm x 1cm and were weld from one side to a copper wire used for electric connection. Two methods are in general use for the determination of the corrosion current density (i_{corr}), which is a measure of corrosion rate. These methods are Stern-Geary [3] method and intercept [4] method and they are based on anodic and/ or cathodic Tafel curves. Stern-Geary method used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives log i_{corr} and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of inhibitor. Then I_{corr} was used for calculation of inhibition efficiency and surface coverage (θ).

$$\% \text{ IE} = [1 - (i_{corr\,(inh)} / i_{corr\,(free)})] \times 100 \qquad (4)$$

$$\theta = [1 - (i_{corr\,(inh)} / i_{corr\,(free)})] \qquad (5)$$

where $i_{corr\,(free)}$ and $i_{corr\,(inh)}$ are the corrosion current densities in absence and presence of inhibitors.

3. RESULTS AND DISCUSSION

3.1. Corrosion inhibition behavior

Figure (1) shows the weight loss- time curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e) at 30°C. It is observed from the Figure that the weight loss decreased, and therefore the corrosion inhibition strengthened, with increase in inhibitor concentration. This trend may result from the fact that adsorption and surface coverage increases with the increase in concentration. Thus the surface is efficiently separated from the medium [8]. The linear variation of weight loss with time in uninhibited and inhibited 1 M HCl indicates the absence of insoluble surface films during corrosion. Tables 2 shows that %IE increases with increase in inhibitor concentration. The %IE for different investigated compounds increases in the following order a > b > c > d > e.

Table 2. % IE at different concentrations of pharmaceutical compounds for the corrosion of aluminum after 120 minutes immersion in 1 M HCl at 30°C.

Concentration M	% Inhibition (% IE)				
	(a)	(b)	(c)	(d)	(e)
1×10^{-6}	56.5	65.6	70.5	76.2	77.0
3×10^{-6}	65.6	67.2	70.6	77.1	79.5
5×10^{-6}	67.2	68.9	77.0	72.9	80.3
7×10^{-6}	69.7	69.7	78.2	78.6	82.8
9×10^{-6}	70.5	71.2	79.5	78.7	83.6
11×10^{-6}	71.3	71.3	79.5	81.1	86.9

3.2. Synergistic effect

Fig. (2) shows the weight loss- time curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e) with addition of 10^{-2}M of KI. Table

3 gives the values of %IE for different concentrations of investigated surfactant compounds and 10^{-2}M KI. The addition of KI improves the %IE of the investigated compounds significantly. The synergistic effect between Investigated compounds and KI is due to interactions between chemisorbed I^- and organic compunds.The stabilization of adsorbed organic cations on the surface, which may be exhibited by electrostatic interactions with I^- ions, leads to higher surface coverage and greater corrosion inhibition.

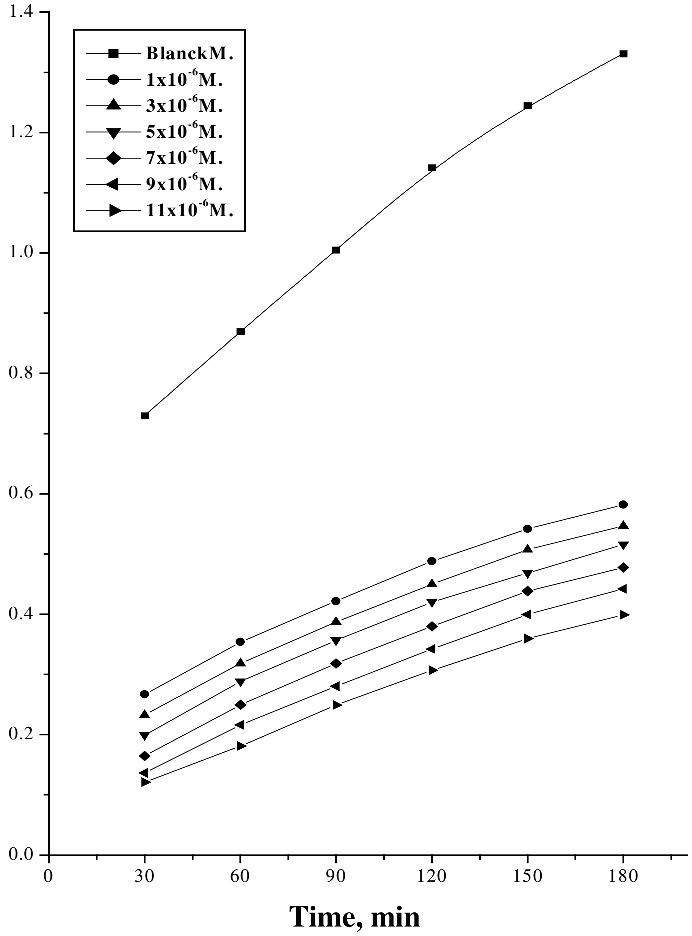


Figure 1. Weight loss- time curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e) at 30^{o}C.

Table 3. % IE at different concentrations of the investigated surfactant compounds with addition of 10^{-2}M KI for the corrosion of aluminum after 120 minutes immersion in 1M HCl at 30^{o}C.

Concentration M	% Inhibition Efficiency (%IE)				
	(a)	(b)	(c)	(d)	(e)
1×10^{-6}	79.4	79.5	80.3	83.6	85.2
3×10^{-6}	81.1	82.0	83.5	84.4	85.3
5×10^{-6}	81.7	82.8	83.6	84.4	85.4
7×10^{-6}	82.6	83.1	84.3	85.7	87.7
9×10^{-6}	83.6	83.6	86.1	86.1	87.8
11×10^{-6}	85.2	85.2	86.9	87.7	90.9

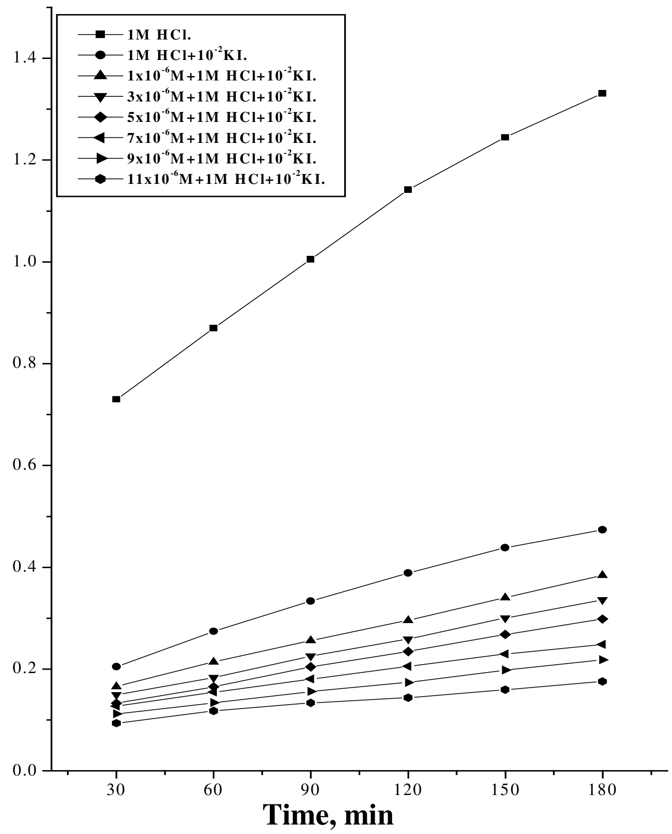


Figure 2. Weight loss- time curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e) without and with addition of 1x10^{-2}M KI at 30°C.

Table 4. Synergism parameter (S) for different concentrations of investigated surfactant compounds with addition of 1x10^{-2}M KI for the corrosion of aluminum after 120 minutes immersion in 1M HCl at 30°C.

Concentration M	Synergism parameter (S_θ)				
	(a)	(b)	(c)	(d)	(e)
1×10^{-6}	0.956	1.007	1.076	1.123	1.157
3×10^{-6}	0.974	1.016	1.081	1.124	1.176
5×10^{-6}	0.990	1.022	1.084	1.140	1.196
7×10^{-6}	1.000	1.028	1.092	1.146	1.213
9×10^{-6}	1.007	1.040	1.102	1.151	1.231
11×10^{-6}	1.036	1.063	1.107	1.158	1.263

The interaction of inhibitor molecules can be described by introducing of an parameter, S_θ, obtained from the surface coverage values (θ) of the anion, cation and both. Aramiki and Hackerman [9] calculated the synergism parameter, S_θ, using the following equation.

$$S_\theta = 1-\theta_{1+2}/\ 1-\theta'_{1+2} \qquad (6)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, $\theta_1 =$ surface coverage by anion, $\theta_2 =$ surface coverage by cation and $\theta'_{1+2} =$ measured surface coverage by both the anion and the cation, which may be attributed to competitive adsorption as can be see from table (4), S_θ values nearly equal to unity which suggests that the enhanced inhibition efficiencies caused by the addition of these anions to surfactants is due to mainly to the synergistic effect.

3.3. Adsorption Isotherm

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior [10]. The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from weight-loss data. Data were tested graphically by fitting to various isotherms. A plot of log θ vs. log C for the surfactant compounds. (Fig.3) suggesting that the adsorption of these compounds on the Al surface follows the Freundlish adsorption isotherm which obeys the relation[11]:

$$\log \theta = \log k + n \log C \ (0 < n < 1) \qquad (7)$$

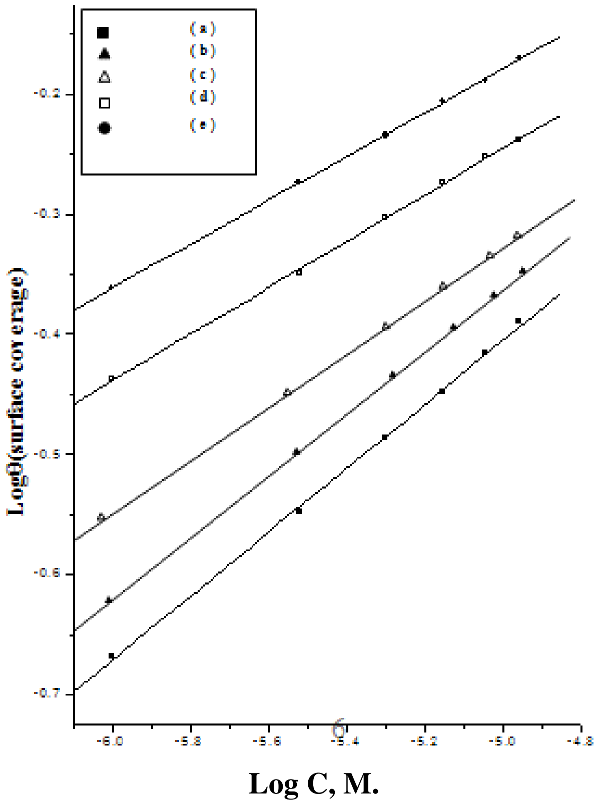


Figure 3. Curve fitting of corrosion data for aluminum in 1M HCl in presence of different concentrations of the surfactant compounds to Freundlish adsorption isotherm at 30°C.

Plots of log θ vs log C for adsorption of the surfactant compounds on the surface of aluminum in 1M HCl at 30°C are shown in Fig. (3). The data gave straight lines of intercept log K and slope n indicating that Freundlish adsorption isotherm is valid for these compounds. From this figure the order of decreasing inhibition efficiency of the surfactant compounds is as follows:

(a) < (b) < (c) < (d) < (e)

Table 5. Equilibrium constant and adsorption free energy of the surfactant compounds adsorbed on aluminum surface.

K	$-\Delta G_{ads}$ kJ. mol^{-1}	Inhibitors
16.51×10^{-2}	5.52511	(a)
18.44×10^{-2}	5.80085	(b)
27.68×10^{-2}	6.81396	(c)
43.12×10^{-2}	7.91958	(d)
48.35×10^{-2}	8.20512	(e)

This table shows that the value of ΔG_{ads} were calculated from the relation[12] :

$$K= 1/55.5 \exp(-\Delta G_{ads})/RT \qquad (8)$$

The standard free energy of adsorption is associated with water adsorption/desorption equilibrium.

It is clear that the value of ΔG_{ads} increases with increasing solvation energy of adsorbed species which in turn increases with increasing the size of the molecule. The negative values of ΔG_{ads} obtained here indicate that the adsorption process of these compounds on the metal surface is spontaneous.

3.4. Effect of temperature

The effect of temperature on the corrosion behavior of Al was studied by weight loss methods at various temperatures in the range 30-50 ^{o}C in the absence and presence of different concentrations of compound (e) in 1M HCl media. and %IE was plot vs. concentration of compound (e) and is shown in Fig. 4. It is obvious that % IE increases with increasing the concentration of compound (e) and decreases with increasing the temperature. This indicated fact that the augmentation of temperature led to the reduction of the inhibitor adsorption and then the acceleration of the dissolution process [13].

Plot of log k vs. 1/T and log (k/ T) vs. 1/ T for aluminum in 1M HCl in absence and presence of various concentrations of compound (e) is shown in Figs. (5) and (6), respectively. as shown from Figure (5), straight lines were obtained according to Arrhenius equation: and transition state equation

$$k=A \exp (- E_a^*/ RT) \qquad (9)$$

where k is the corrosion rate, A is a constant depends on a metal type and electrolyte, E_a^* is the apparent activation energy, R is the universal gas constant and T is the absolute temperature.

$$\text{Rate} = RT/ Nh \exp (\Delta S^*/ R) \exp (-\Delta H^*/ RT) \qquad (10)$$

where h is Planck's constant, N is Avogadro's number, ΔH^* is the activation enthalpy and ΔS^* is the activation entropy. The calculated values of the apparent activation energy, E_a^*, activation enthalpies, ΔH^* and activation entropies, ΔS^* are given in Table (6). These values indicate that the presence of the additives increases the activation energy, E_a^* and the activation enthalpy, ΔH^* and decreases the activation entropy, ΔS^* for the corrosion process. The addition of inhibitors modified the values of Ea^*. This is may be attributed to the adsorption of inhibitors on Al surface.,

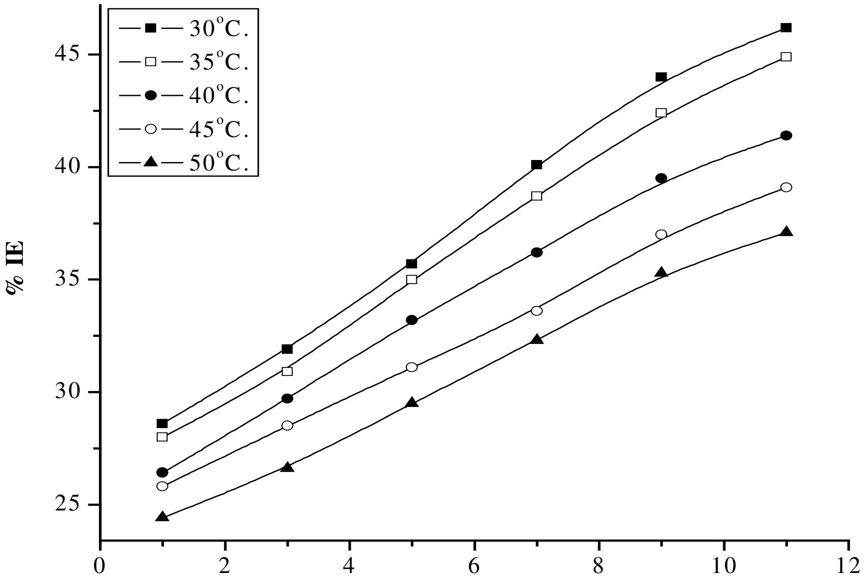


Figure 4. Variation of the inhibition efficiency (% IE) with the concentration of compound (e) at different temperatures.

Table 6. Activation parameters of the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e).

Inhibitors	Activation parameters		
	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J mol^{-1}K^{-1}
Free acid	58.48	56.22	163.22
(a)	62.22	59.54	158.44
(b)	62.85	60.29	155.05
(c)	63.12	61.49	153.70
(d)	63.55	62.32	151.35
(e)	63.96	62.96	150.30

and this adsorption make an energy barrier and this energy barrier of corrosion reaction increases as the concentration of the inhibitor is increased., and hence %IE increases. This suggested that the process is activation controlled. Since the activation energy value of 63.96kJ mol^{-1} (Table 6) for HCl–inhibitor systems support the fact that the inhibitors are physically adsorbed on Al surface. This is in agreement with reports of Abiiola et.al [14], Ebenso et.al [15] ,Ebenso [16] and Barrow [17] according to these reports Ea*due to chemical adsorption (>80 kJ mol^{-1}) is considerably larger than due to physical adsorption(<80 kJ mol^{-1})the increase in the activation enthalpy (ΔH*) in presence of the inhibitors implies that the addition of the inhibitors to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent depends on the type and concentration of the present inhibitor. The entropy of activation (ΔS*) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step [18-20].

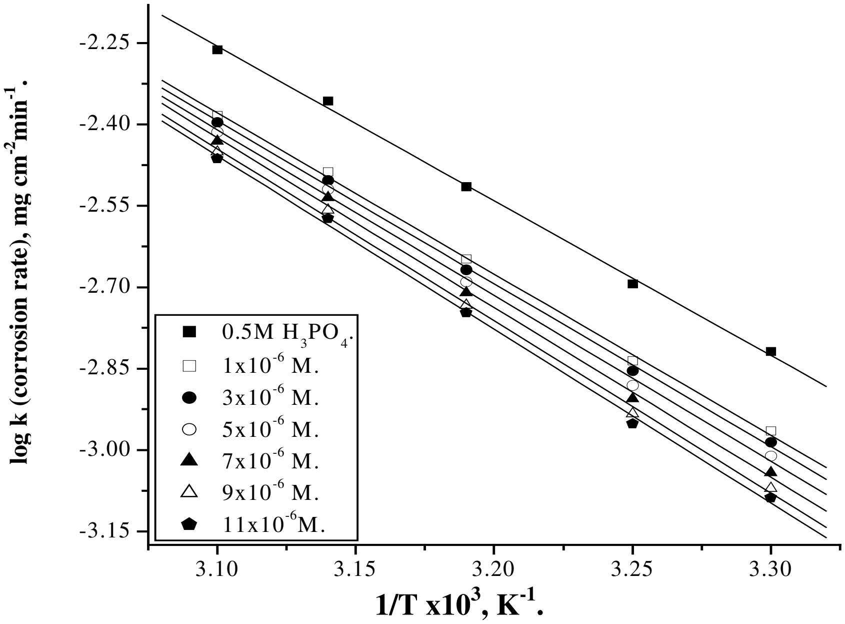


Figure 5. log corrosion rate- 1/T curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e).

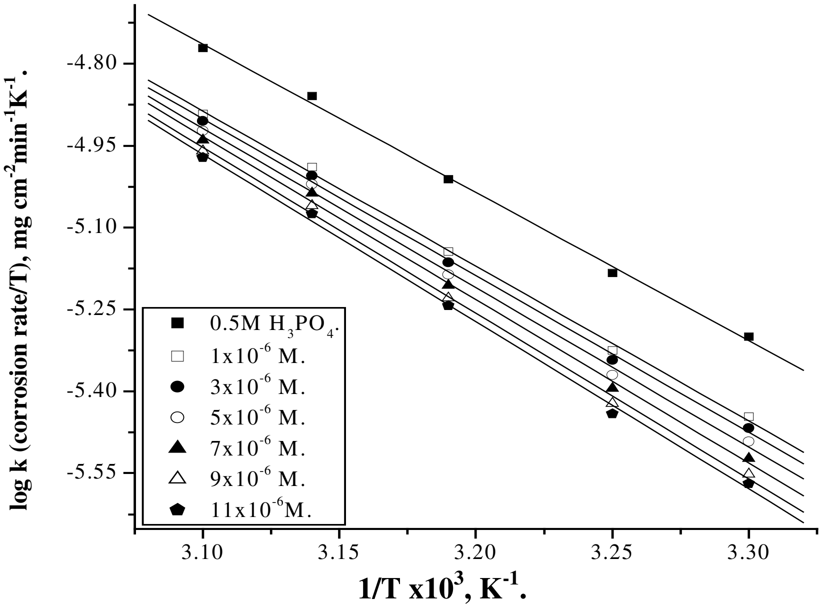


Figure 6. log (corrosion rate/T)- (1/T) curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e).

3.5. Electrochemical measurement

3.5.1. Tafel method

Figure (7) shows typical current-potential of Al in 1 M HCl in the absence and presence of various concentrations of compound e. values of associated electrochemical parameters such as current density ($i_{corr.}$), corrosion potential ($E_{corr.}$), Tafel slopes (β_a and β_c), and corrosion inhibition efficiency (per cent) as function of compound e concentrations in 1 M HCl are given in Table (7). From this Table. It is evident from this Table that the Tafel constants β_a and βc did not change significantly. It observed from the Tafel curve that the inhibitor was mixed type because they enhance was the anodic and cathodic processes but the anode is more polarized when an external current was applied. Addition of surfactant compounds increased both cathodic and anodic over voltage and caused mainly parallel displacement to the more negative and positive respectively.

- The corrosion current density (i_{corr}) decreases with increasing the concentration of surfactant compounds, which indicates that the presence of these compounds retards the dissolution of aluminum in 1M HCl and the degree of inhibition depends on the concentration.
- The values of corrosion potential (E_{corr}) values shifted to less negative values by increasing the concentration of surfactant compounds.

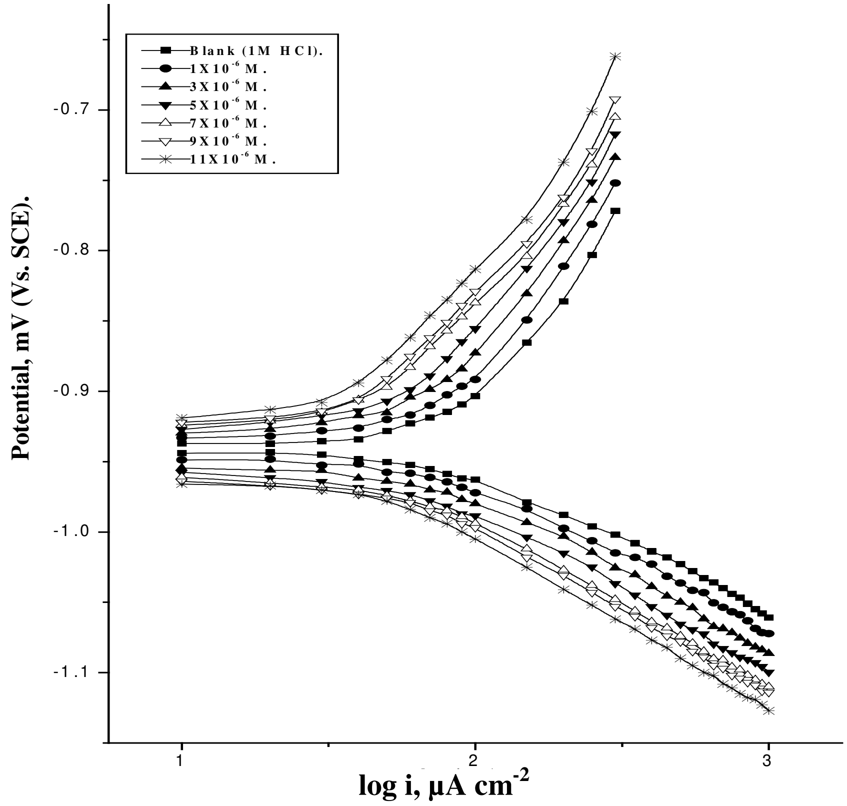


Figure 7. Galvanostatic polarization curves for the corrosion of aluminum in 1M HCl in absence and presence of different concentrations of compound (e) at 30°C.

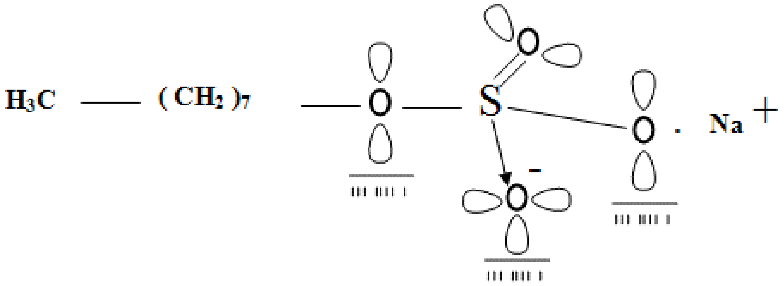
Table 7. The effect of concentrations of compound (e) on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a& β_c), %inhibition efficiency (% IE) and degree of surface coverage (θ) for the corrosion of aluminum in 1M HCl at 30°C.

Conc., M	-E_{corr}, mV	i_{corr}, uA cm^{-2}	-β_c, mV dec^{-1}	β_a, mV dec^{-1}	θ	% IE
0	942	62.0	217	89	-------	-------
1x10^{-6}	938	39.0	207	112	0.782	78.2
3x10^{-6}	937	36.8	209	114	0.807	80.7
5x10^{-6}	936	34.1	211	116	0.815	81.5
7x10^{-6}	935	31.2	212	118	0.839	83.9
9x10^{-6}	934	30.3	214	120	0.848	84.8
11x10^{-6}	933	26.6	215	123	0.881	88.1

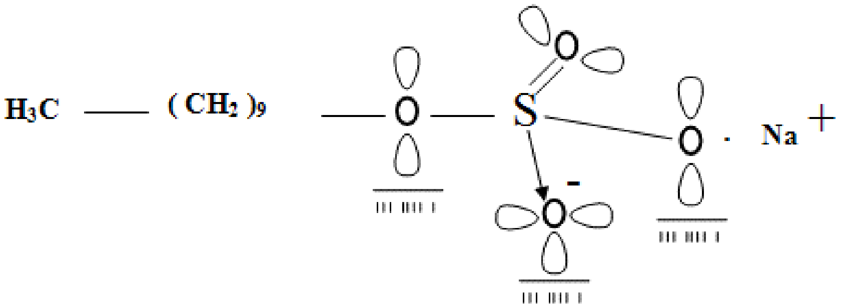
3.6. Chemical structure of the inhibitors and its effect on the corrosion inhibition.

Skeletal representation of the proposed mode of adsorption of the of the investigated surfactant compounds is shown in Fig. (8). The order of decreasing inhibition efficiency of these tested compounds is (a) < (b) < (c) < (d) < (e).

For these compounds on the basis of the molecular size and the number of adsorption centers, compound (e) should be the most effective inhibitors, inspite of it has two active adsorption centers. The highest inhibition efficiency may be due to : (a) higher molecular size and (b) benzene ring contributes π electrons to the adsorption centers and hence increases the electron density on the adsorption centers. Compounds b < c < d in percentage inhibition efficiency and this is agrees with their molecular size.



(a)



(b)

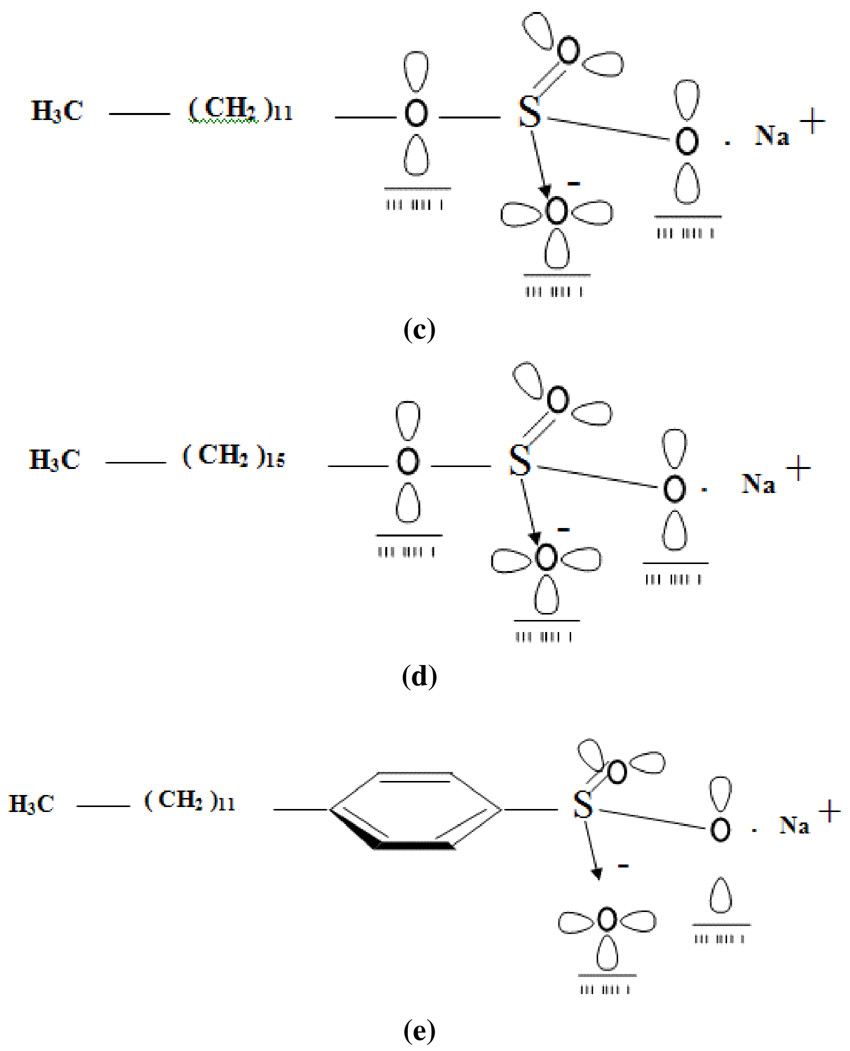


Figure 8. Skeletal representation of the mode of adsorption of the investigated surfactant compounds.

4. CONCLUSIONS

- The investigated surfactant compounds act as inhibitors for the corrosion of aluminum in hydrochloric acid acid solution.
- Surfactant compounds adsorb on Al surface according to the Freundlich adsorption isotherm.
- The inhibitors increase the value of activation energy of corrosion and consequently, decrease the rate of dissolution of aluminum in HCl solution.
- Polarization data showed that these investigated surfactant compounds acted as mixed-type inhibitors.
- The inhibition efficiencies obtained from polarization and weight loss measurements are in good agreement with each other.

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